COVER SHEET

Raman spectroscopy of selected lead minerals of environmental significance

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Abstract

The Raman spectra of the minerals cerrusite ($PbCO_3$), hydrocerrusite ($Pb_2(OH)_2CO_3$), phosgenite ($Pb_2CO_3Cl_2$) and laurionite (Pb(OH)Cl) have been used to qualitatively determine their presence. Laurionite and hydrocerrusite have characteristic hydroxyl stretching bands at 3506 and 3576 cm^{-1}. Laurionite is also characterised by broad low intensity bands centred at 730 and 595 cm^{-1} attributed to hydroxyl deformation vibrations. The minerals cerrusite, hydrocerrusite and phosgenite have characteristic CO (ν_1) symmetric stretching bands observed at 1061, 1054 and 1053 cm^{-1}. Phosgenite displays complexity in the CO (ν_3) antisymmetric stretching region with bands observed at 1384, 1327 and 1304 cm^{-1}. Cerrusite shows bands at 1477, 1424, 1376 and 1360 cm^{-1}. The hydrocerrusite Raman spectrum has bands at slightly different positions from cerrusite with bands at 1479, 1420, 1378 and 1365 cm^{-1}. The complexity of the ν_3 region is also reflected in the ν_2 and ν_4 regions with the observation of multiple bands. Laurionite is characterized by two intense bands at 328 and 272 cm^{-1} attributed to PbO and PbCl stretching bands. Importantly all four minerals are characterized by their Raman spectra enabling the mineral identification in leachates and contaminates of environmental significance.

Key Words- lead, chloride, carbonate, Raman spectroscopy, laurionite, phosgenite, cerrusite, hydrocerrusite.

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1. Introduction

The environmental aspects of mineral solution chemistry for the evolution of secondary minerals are becoming increasingly important. [1-4]Old mine sites that even date back to Roman times such as at Laurion in Greece [5]are subject to corrosion on exposure to air or to sea water. These induced chemical reactions result in the formation of many products, many of which are environmentally hazardous. Many of the secondary minerals of both lead and copper belong to this category. Lead compounds are particularly dangerous because of their solubility in ground waters and also their significant volatility. This makes the many products of the patination of slag heaps of importance for chemical study. [1, 2, 6] In particular a rapid means of identification of the complex array of lead compounds is of a necessity.

A complex set of equilibria exists for the lead chloride minerals. These minerals include laurionite (PbOHCl), paralaurionite(PbOHCl), penfieldite (Pb_2Cl_3OH), mendipite ($Pb_3O_2Cl_2$), fiedlerite ($Pb_3Cl_4(OH)_2$) and phosgenite ($PbCO_3Cl_2$). The stability of the lead chloride minerals has been assessed. [7, 8] Laurionite and paralaurionite are thermodynamically stable minerals over a wide pH and chloride concentration range and the stability range is between that of cotunnite ($PbCl_2$) and mendipite ($Pb_3O_2Cl_2$). Interestingly several of these minerals including laurionite, paralaurionite together with cerrusite, hydrocerrusite were use in ancient Egyptian times as cosmetic ingredients. [9-11] Whilst X-ray diffraction has been used extensively for the identification of the mineral structures for a considerable period of time[4, 12-16], it is apparent that very few vibrational spectroscopic analyses of these minerals has been forthcoming. More particularly there is a lack of any Raman spectroscopic studies of these minerals especially laurionite. In this research we report the analytical measurement of phosgenite, cerrusite, hydrocerrusite and laurionite. The significance of these lead minerals is that they are mixed anionic species. The minerals are amongst the most predominant minerals in the leaching products of slag dumps.

2. Materials and methods

2.1 Minerals:

Cerrusite was obtained from the Rum Jungle Mine, Northern Territory, Australia. Hydrocerrusite (with cerrusite) was obtained from Mineralogical research Company and the sample originated from the C. & B. mine Gila County, Arizona, USA. Laurionite originated from Laurion, Greece and was obtained from the South Australian Museum registered number G11834. Phosgenite was obtained from the South Australian Museum and was registered number G12013. The phosgenite was originally sourced from Monteponi, Sardinia, Italy. Sample registered number D191881 Phosgenite was obtained from Consols mine, Broken Hill SA.

2.2 Raman microprobe spectroscopy

The crystals of the minerals were placed and orientated on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10x

and 50x objectives. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a Charge Coupled Device (CCD). Raman spectra were excited by a Spectra-Physics model 127 He-Ne laser (633 nm) at a resolution of 2 cm^{-1} in the range between 100 and 4000 cm^{-1}. Spectra were accumulated using the highest magnification to improve the signal to noise ratio and were calibrated using the 520.5 cm^{-1} line of a silicon wafer. Spectra at liquid nitrogen temperature were obtained using a Linkam thermal stage (Scientific Instruments Ltd, Waterfield, Surrey, England).

2.3 Infrared spectroscopy

Infrared spectra were obtained using a Nicolet Nexus 870 FTIR spectrometer with a smart-endurance single-bounce diamond ATR cell. Spectra over the 4000 to 525 cm^{-1} range were obtained by the co-addition of 64 scans with a resolution of 4 cm^{-1} and a mirror velocity of 0.6329 cm/s.

Spectroscopic manipulation such as baseline adjustment, smoothing and normalisation were performed using the Spectracalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel 'Peakfit' software package, which enabled the type of fitting function to be selected and allows specific parameters to be fixed or varied accordingly. Band fitting was performed using a Gauss-Lorentz cross-product function with the minimum number of component bands used for the fitting process. The Gauss-Lorentz ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of r^2 greater than 0.995.

3. Results and discussion

In the environment of lead slag heaps the following reactions can occur:

$Pb + 1/2O_2 \rightarrow PbO$ (litharge)
$PbO + CO_2 \rightarrow PbCO_3$ (cerrusite)
$2PbO + H_2O + CO_2 \rightarrow Pb_2(OH)_2CO_3$ (hydrocerrusite)
$2PbO + H_2O + 2Cl^- \rightarrow 2Pb(OH)Cl$ (laurionite)
$2PbO + CO_2 + 2\ Cl^- \rightarrow Pb_2CO_3Cl_2$ (phosgenite)

These minerals are readily formed in lead slag dumps. Other more complex minerals such as diaboléite, cumengéite and boléite may also form. The minerals cerrusite and hydrocerrusite have similar appearances as do laurionite and phosgenite. This makes the visual identification of the minerals in slag heaps difficult.

3.1 Raman spectroscopy

Of the four minerals studied in this work only two, namely hydrocerrusite and laurionite have hydroxyl groups in their structure. Figure 1 displays their Raman spectra. Factor group analysis predicts one Raman-active and one infrared-active vibration. Only a single Raman band at 3506 cm^{-1} was observed. No comparison could be made with published data as none was found. The observation of a single Raman band is in harmony with the crystal structure of laurionite. The Raman spectrum of hydrocerrusite displays two bands at 3576 and 3536 cm^{-1}. Infrared bands

are observed at 3574 and 3535 cm^{-1}. These two bands are assigned to the in-phase and out-of-phase vibrations of the OH unit. Farmer suggested that the ν_1 and ν_3 bands were coincident at 3535 cm^{-1} [17]. In this work we suggest that the two stretching modes occur at different wavenumbers and that the band at 3535 cm^{-1} is that of the symmetric stretching vibration.

The Raman spectra of the CO stretching region of cerrusite, hydrocerrusite and phosgenite is shown in Figure 2. Phosgenite shows an intense Raman band at 1061 cm^{-1}. The band is not observed in the infrared spectrum. The band is assigned to the CO symmetric stretching vibration. Griffith reported a band at 1053 cm^{-1} and attributed the band to the symmetric stretching vibration. [18] The Raman spectrum of cerrusite displays an intense band at 1054 cm^{-1} with a very low intensity band at 1031 cm^{-1}. The infrared spectrum shows a band at 1055 cm^{-1}. This band is attributed to the CO stretching vibration of cerrusite. The Raman spectrum of hydrocerrusite shows an intense band at 1053 cm^{-1} with a low intensity band at 1031 cm^{-1}. There is a difference in the band centers for each of the three minerals of interest and this difference could be used to qualitatively identify the minerals in complex mixtures.

The Raman spectra of the antisymmetric stretching region of phosgenite, cerrusite and hydrocerrusite are displayed in Figure 3. Phosgenite displays complexity in this spectral region with bands observed at 1384, 1327 and 1304 cm^{-1}. A fourth component was curve resolved at 1293 cm^{-1}. Low intensity bands were also observed at 1672 and 1518 cm^{-1}. Farmer reported bands in this region at 1510 and 1350 cm^{-1}. The Raman spectrum of cerrusite in this spectral region shows bands at 1477, 1424, 1376 and 1360 cm^{-1}. Farmer suggested a single broad band centered at 1410 cm^{-1}. [17] The Raman spectrum of hydrocerrusite shows bands at 1479, 1420, 1378 and 1365 cm^{-1}. The Raman spectrum of hydrocerrusite displays overlap of the 1378 and 1365 cm^{-1} whereas the bands are well separated in the spectrum of cerrusite. Farmer reported bands at 1430, 1400 and 1360 cm^{-1} for hydrocerrusite. [17]

The Raman spectra of the 600 to 800 cm^{-1} region of the four minerals of environmental significance are shown in Figure 4. The Raman spectrum of laurionite displays a broad band centred upon 730 cm^{-1}. This band is assigned to the hydroxyl deformation mode. A second broad band is also observed centred at 595 cm^{-1}. This band is also assigned to a hydroxyl deformation mode. The Raman spectrum in the 600 to 800 cm^{-1} region of phosgenite displays two Raman bands at 667 and 650 cm^{-1}. Infrared spectra display two bands at 760 and 650 cm^{-1}. The values are in good agreement with published data [17].

The Raman spectrum of cerrusite shows a set of bands with band centres at 694, 681, 674 and 667 cm^{-1}. Griffith reported the Raman spectrum of cerrusite and observed bands at 698, 685 and 678 cm^{-1}. [19] The bands were attributed to the A_{1g}, B_{2g} and B_{1u} modes. In this work we find an additional band at 667 cm^{-1}. The infrared spectrum shows a single intense band at 677 cm^{-1}. The Raman spectrum of hydrocerrusite shows four bands at 695, 680, 674 and 669 cm^{-1}. Our infrared spectrum shows an intense band at 675 cm^{-1}. Farmer reported bands at 700, 687 and 676 cm^{-1} in this spectral region [17].

The low wavenumber region of the Raman spectra of phosgenite, laurionite and hydrocerrusite are shown in Figure 5. This region is important for using Raman

spectroscopy to distinguishing between the minerals. The Raman spectrum of laurionite shows two strong bands at 328 and 272 cm^{-1}. Raman bands are also observed at 174, 142 and 131 cm^{-1}. The latter band shows significant intensity. The Raman spectrum of phosgenite in this region displays bands at 182 and 176 cm^{-1} with other low intensity bands observed at 282 and 152 cm^{-1}. Bands are observed for hydrocerrusite 417, 391, 376, 318, 221, 177 and 152 cm^{-1}. A significant number of bands are observed for cerrusite and are listed in Table 1.

4. Conclusions

Raman spectroscopy has been used to analyse a set of minerals of environmental significance. The minerals are readily identified by their Raman spectra. Such minerals as cerrusite, phosgenite and laurionite are of archaeological significance in that the minerals were used by the ancient Egyptians for cosmetics. Raman spectroscopy enables the rapid identification of these minerals and may serve as a more efficient technique for the analysis of mixtures of these minerals.

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Table 1 Wavenumbers of bands in the Raman and infrared spectral results of cerrusite, hydrocerrusite, phosgentite and laurionite

Cerrusite $PbCO_3$					**Band assignments of cerrusite**	**Hydro-Cerrusite $Pb_3(CO_3)_2(OH)_2$**			**Phosgenite $Pb_2CO_3Cl_2$**			**Laurionite Pb(OH)Cl**
Raman (This work)	**Raman [18]**	**IR (This work)**	**IR Pub**	**IR Pub [17]**		**Raman**	**IR**	**IR Pub [17]**	**Raman**	**IR**	**IR Pub [17]**	**Raman**
						3576 3536	3574 3535	 3535				3506
			1740	1750		1736 1705 1679	1731		1672	1672 1616		
1477 1424	1484	1440 1404	1460 1405		ν_3 (B_{1u},A_g)	1479 1420	1446	1430 1400 1360	1518		1575 1518	
1376	1369			1420	B_{2g}	1378 1475	1381				1350	
1360					B_{3u}, B_{1g}	1365			1384 1327 1304 1293	1379		
1054 1031	1053	1055	1055	1045	ν_1 (B_{1u},A_g)	1053 1031	106	1090	1061 (ν_1) 1058 (ν_1)			
838 825 815		841	841 826		ν_2 (B_{1u}, A_g)	887 866 837	 834	 850 834	833	840	838	
694	698 685 678	677	689	690 682 670	ν_4 (B_{1u},A_g)	737		700 687 676	 665 650	765 650	760 653	730

681 674					B_{2g}	694 681 671	675					
669					B_{3g}							594
470 396 380						417 391 376						
						318			282			328 272
244 233 227 217 175 147 145 131						221 177 152			182 176 152			174 142 131

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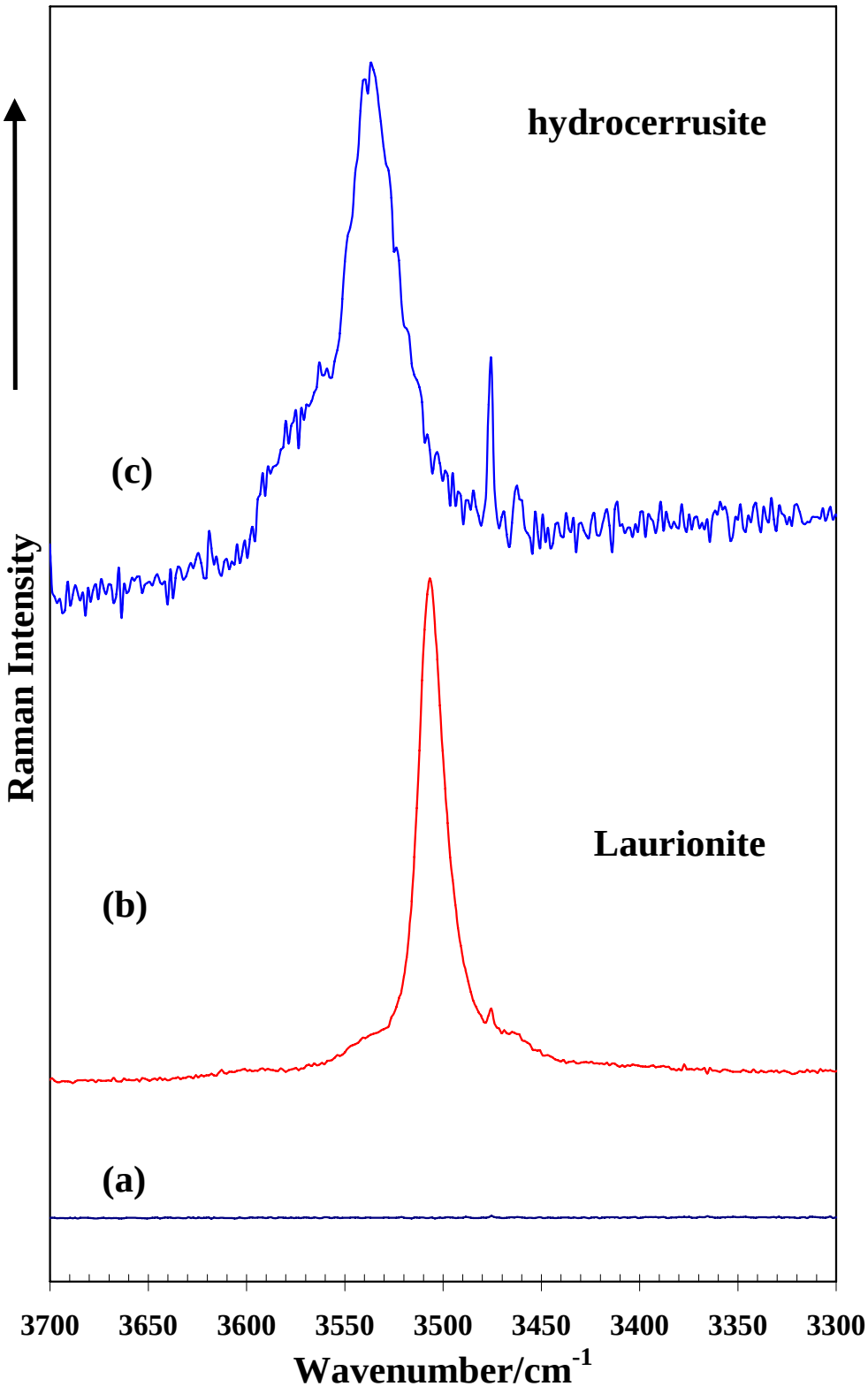
hydrocerrusite
(c)
Raman Intensity
Laurionite
(b)
(a)
3700
3650
3600
3550
3500
3450
3400
3350
3300
Wavenumber/cm-1

Figure 1

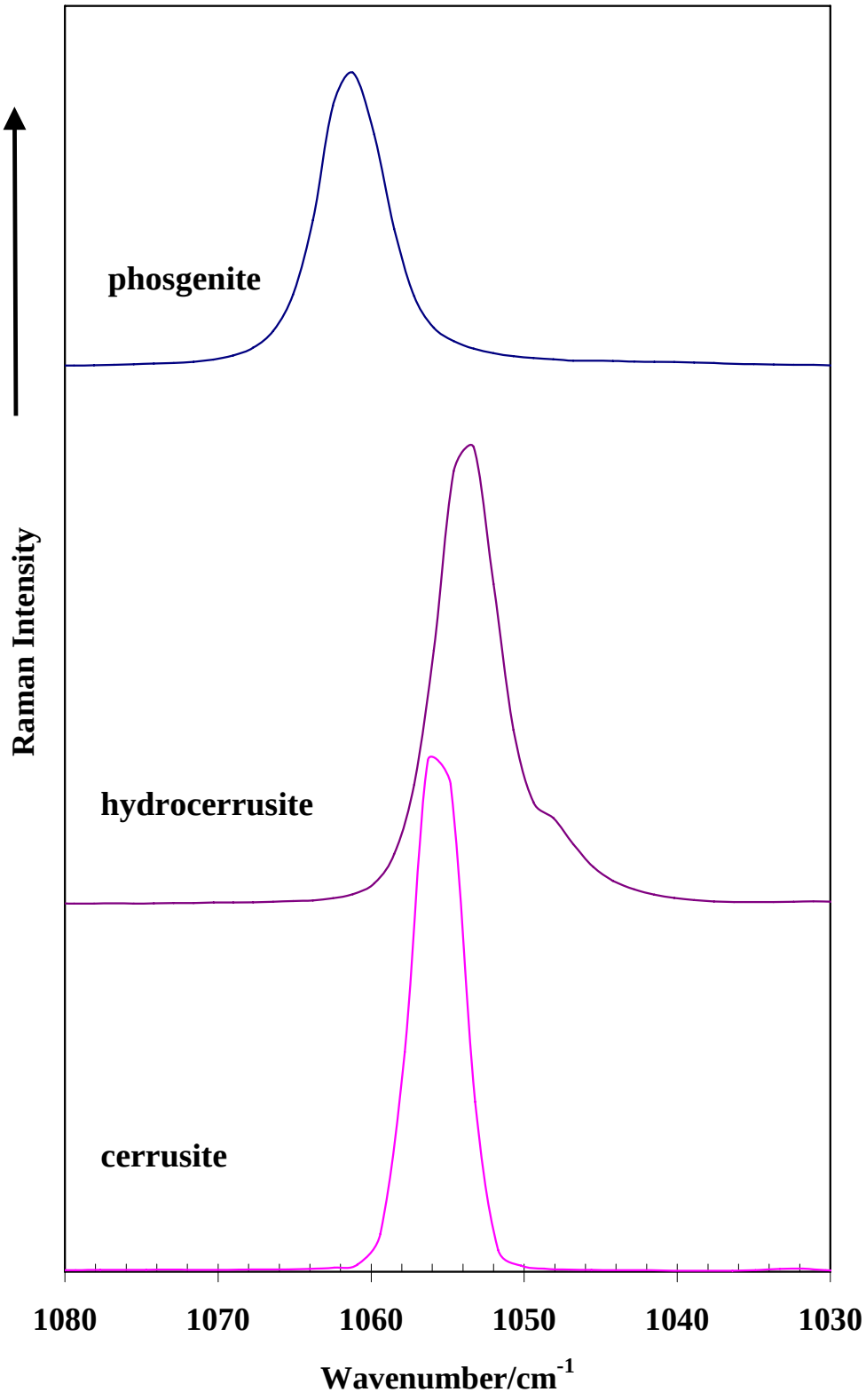
phosgenite
hydrocerrusite
cerrusite
Raman Intensity
1080
1070
1060
1050
1040
1030
Wavenumber/cm-1

Figure 2

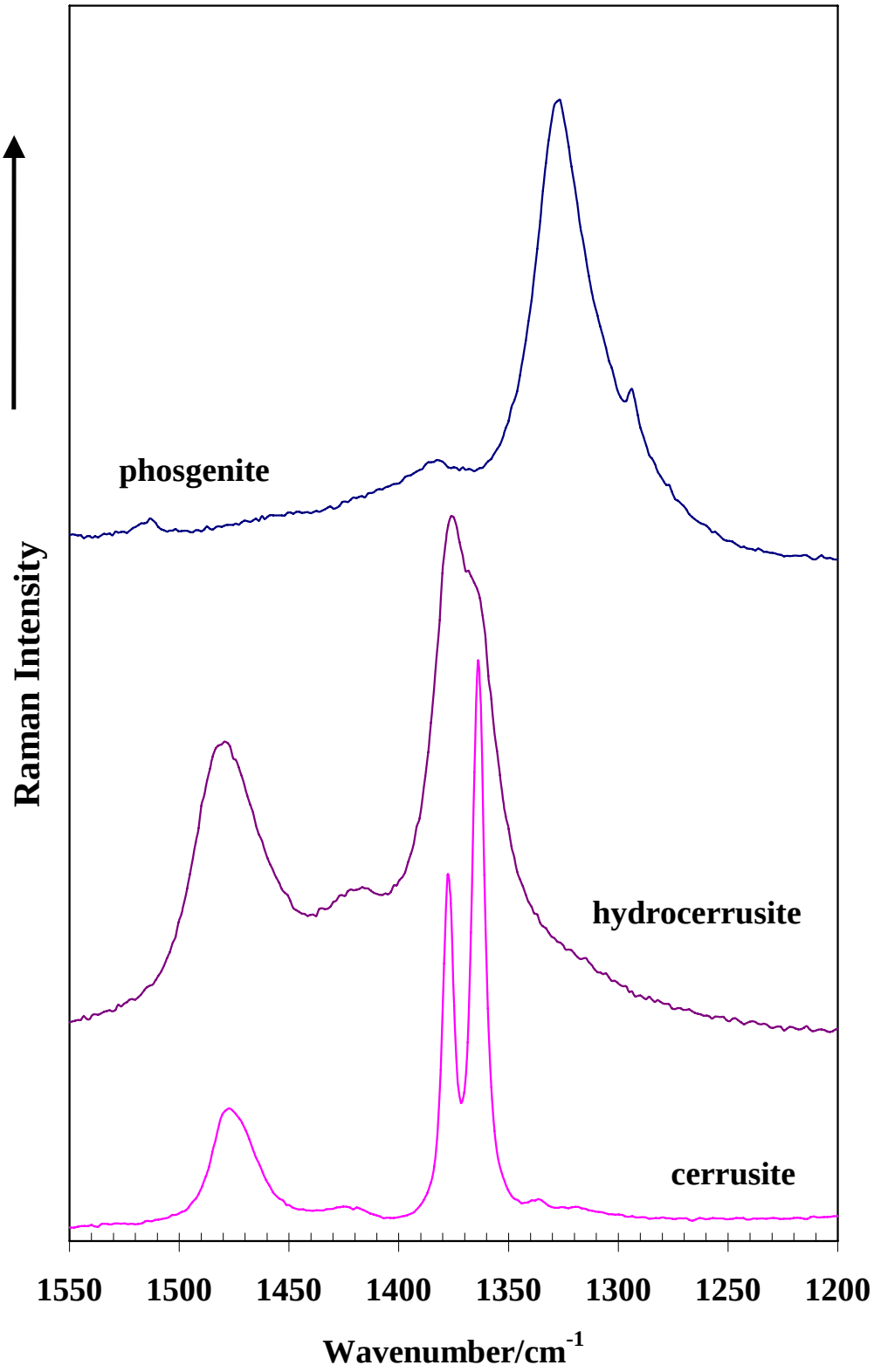
phosgenite
hydrocerrusite
cerrusite
Raman Intensity
1550
1500
1450
1400
1350
1300
1250
1200
Wavenumber/cm-1

Figure 3

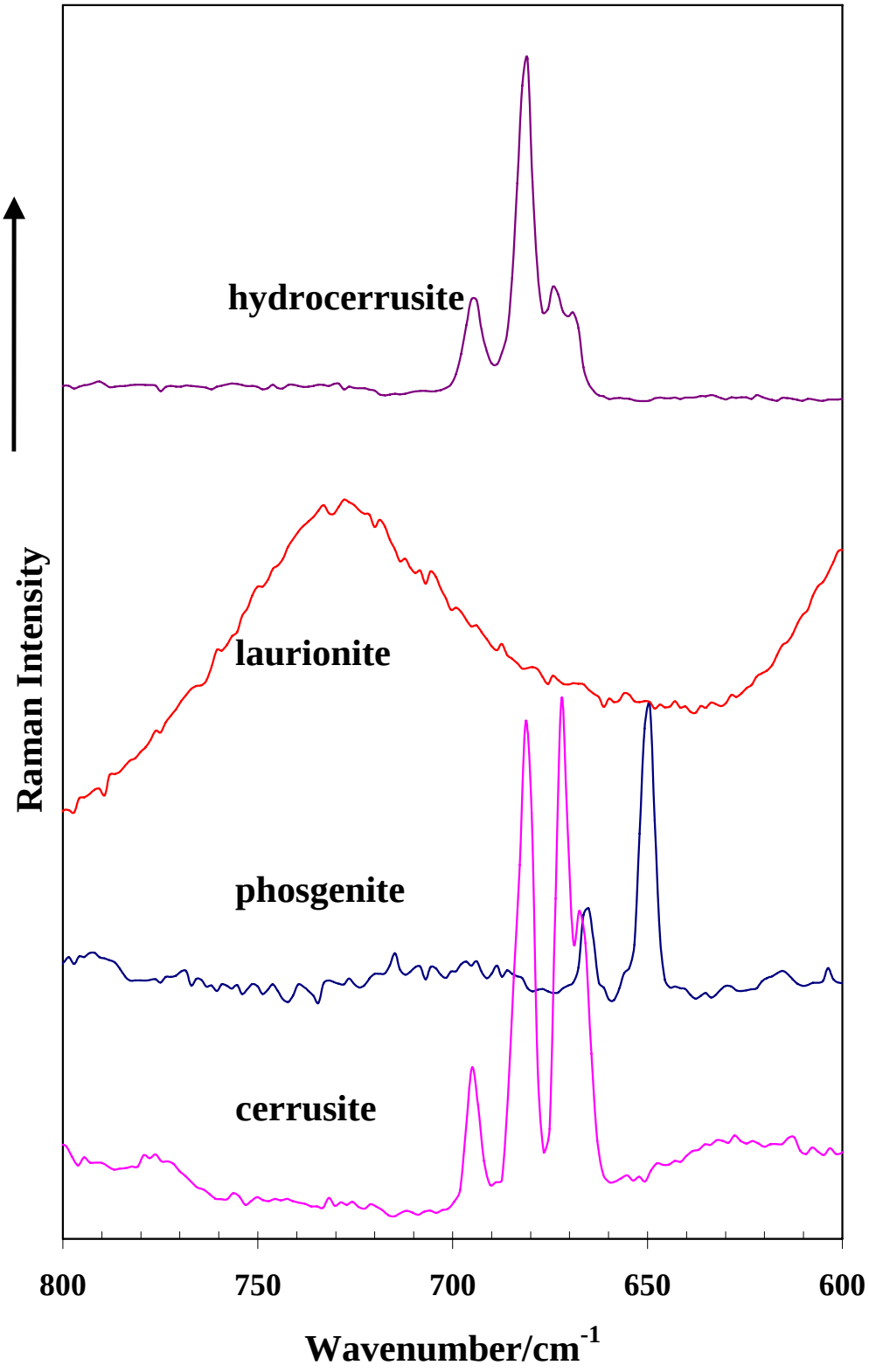
hydrocerrusite
laurionite
phosgenite
cerrusite
Raman Intensity
800
750
700
650
600
Wavenumber/cm-1

Figure 4

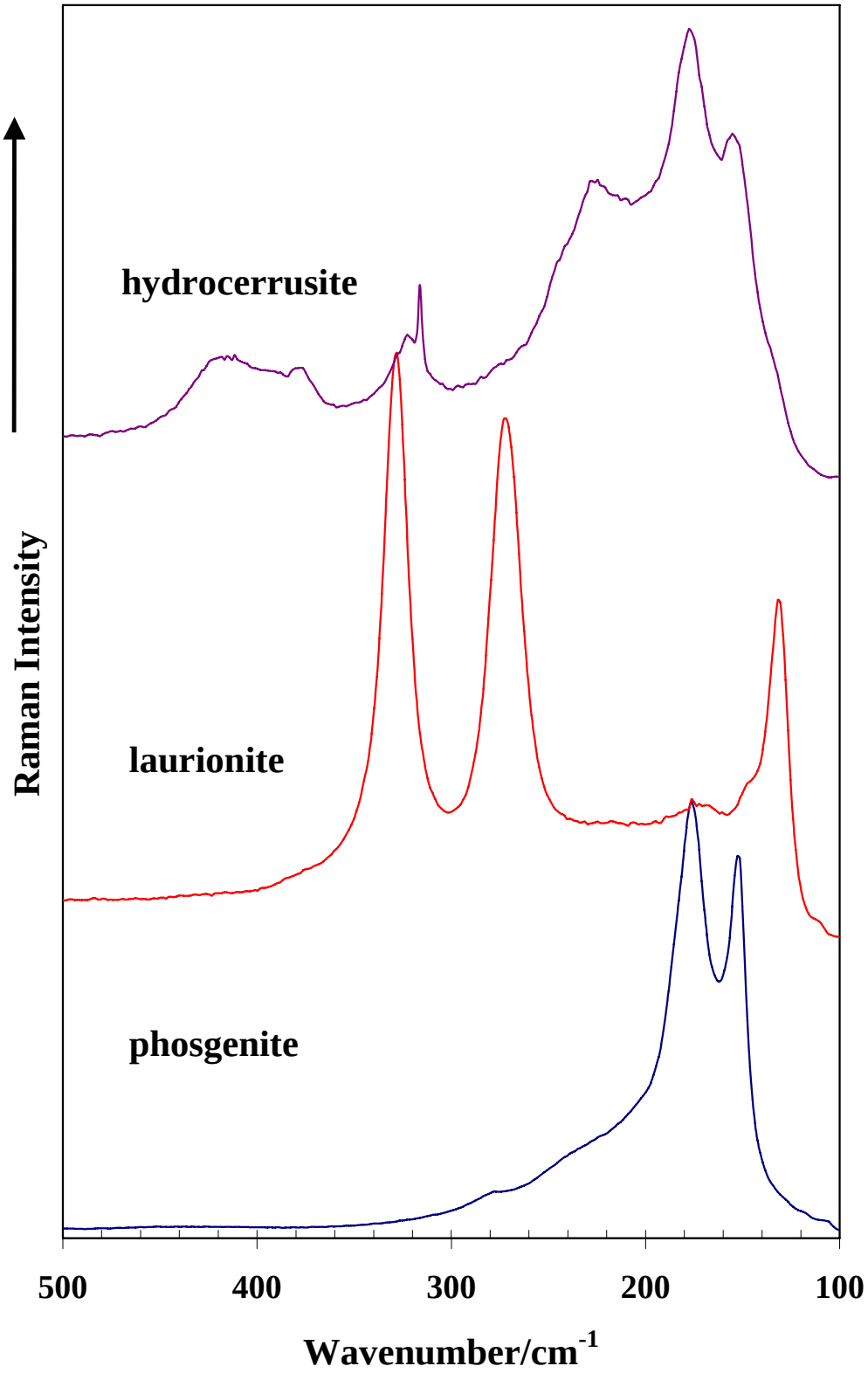
hydrocerrusite
laurionite
phosgenite
Raman Intensity
500
400
300
200
100
Wavenumber/cm-1

Figure 5